

FLAME TEMPERATURES AND VERTICAL GRADIENTS IN NATURAL-GAS FLAMES¹

H. H. KAVELER² AND BERNARD LEWIS

*Explosives Division, Pittsburgh Experiment Station, U. S. Bureau of Mines,
Pittsburgh, Pennsylvania*

Received August 12, 1937

The purpose of the experiments described in this paper was to obtain information on the state of the burnt gas that emerges from a flame by comparing observed maximum flame temperatures determined by the sodium line-reversal method with calculated theoretical temperatures, and by investigating very carefully the nature of the temperature gradients in the vertical direction above the cones of suitably constructed stationary flames.

EXPERIMENTAL METHOD AND PROCEDURE

The accuracy and reliability of the line-reversal method for measuring flame temperatures have been demonstrated by a number of investigators (2) and the method has become standardized. The apparatus used was essentially that employed in previous experiments in this laboratory (1). Some modifications in the details of the apparatus and procedure will be described here.

Two-stage reducing valves with surge chambers of appropriate size were employed to give a steady flow of the gases so that a very steady flame was produced. Air and/or oxygen was passed first through a sodium chloride-vaporizing chamber before entering a mixing chamber. The mixing chamber was a 500-cc. flask in which the natural gas and air or oxygen were premixed before entering the burner.

The composition of the combustible entering the burner was determined from two samples (250 cc. each) which were slowly withdrawn from the mixing chamber. A measurement of temperature gradient usually required thirty minutes, so that one sample was withdrawn during the first

¹ Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

² Assistant chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pennsylvania. Present address: Phillips Petroleum Co., Bartlesville, Oklahoma.

ten minutes and the other during the last ten minutes of this period. The gas was analyzed with a conventional Orsat apparatus. The per cent of oxygen was determined by absorption with pyrogallol reagent up to a concentration of 30 per cent and with chromous acetate reagent when the concentration exceeded this value. Pittsburgh natural gas in the combustible mixture was determined by combustion over a heated platinum wire, the content being determined from the sum of the contraction and carbon dioxide, using a factor determined by careful Orsat analyses of the natural gas. The accuracy of the analyses is 3 per cent or better, as determined by duplicate analyses on each sample taken.

The tungsten-band lamp used in these experiments was aged and calibrated by the manufacturer. The calibration was frequently checked during the course of the work and was found to be constant. The current through the lamp was read to 0.10 ampere, equivalent to $\pm 5^{\circ}\text{C}$. The reversals could be easily read to that limit even for natural gas-oxygen flames for which the reversals become more difficult to follow, owing to the low intensity of the D-radiation from these flames. This is probably due to the suppression of the sodium-atom concentration by the presence of the large excess of oxygen in the gases.

A color correction ($+26^{\circ}\text{C}$.) and a lens correction (-20°C .), as explained elsewhere (1), were applied to the observed temperatures.

AN IMPORTANT EXPERIMENTAL REQUIREMENT

Stationary flames have both vertical and horizontal temperature gradients. The horizontal gradients arise mainly from the interdiffusion of air from the surrounding atmosphere, which causes either secondary combustion or dilution depending upon whether a rich or a lean mixture is being burned. The temperature of the sodium layer nearest the spectroscopist determines, for the most part, the temperature reading. In totally colored flames this sodium layer is greatly affected by such interdiffusion. It was desired to eliminate as far as possible this complicating effect of the horizontal temperature gradient. This could easily be accomplished by coloring only the central part of the flame, so that the temperature observations were confined to presumably isothermal horizontal sections protected from secondary air.

TYPE OF BURNER

In order to obtain centrally colored flames a concentric-tube burner was used. The details of the construction of this burner are shown in figure 1. The outer brass tube of the burner was threaded (40 threads per inch), so that by means of the graduated knurled nut the burner could be moved in the vertical direction.

A number of attempts were made to produce a partially colored single-cone flame over the concentric-tube burner, but the single cone was unstable and vibrated excessively, with a tendency to form a double flame consisting of a cone system on each tube. Temperature observations on partially colored flames were finally made using a nichrome grid. The grid was made from strips of metal 0.5 mm. thick forming a square mesh 2 mm. on edge over the cross section of the burner.

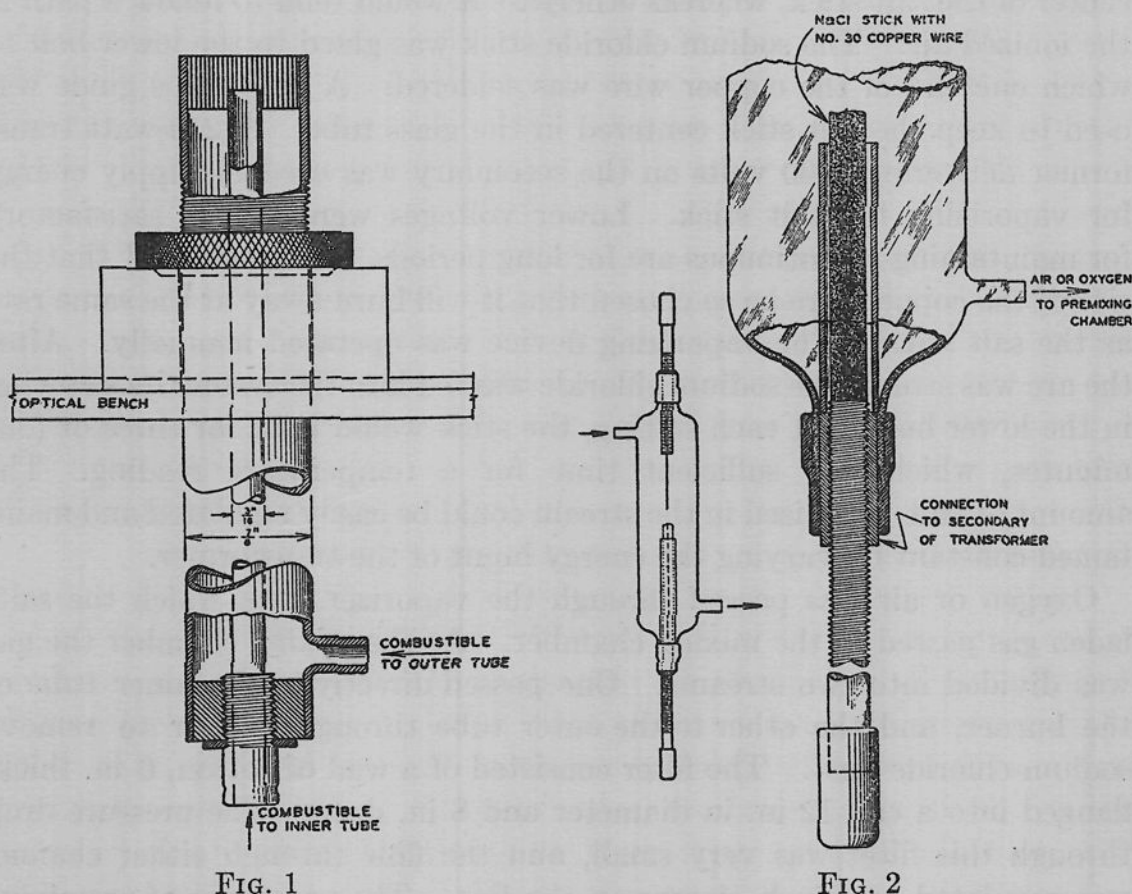


FIG. 1

FIG. 2

FIG. 1. Concentric-tube burner for producing partially colored flames

FIG. 2. Detail of sodium chloride electrode and vaporizer

METHOD OF INTRODUCING SODIUM

The conventional wet method of coloring flames causes water droplets to be introduced into the combustible mixture. In order to eliminate any uncertain effects from this source, we used the following electric-arc method of introducing sodium into the combustible mixtures: A sodium chloride vaporizer, represented in figure 2, was made from a glass tube drawn down to fit brass bushings which were $\frac{3}{8}$ in. by 1 in. and were fastened to the glass by rubber tubing. The electrodes for producing the electric arc were a No. 18 platinum wire and a stick of sodium chloride attached to bolts as shown in the figure. The stick of sodium chloride was $\frac{1}{4}$ in. by 6

in. and was prepared by compressing moistened salt at a pressure of three or four thousand pounds per square inch in a special mold made from two machined steel blocks. The sticks were air-dried for ten days, after which they could be handled without breaking easily. A radial groove was cut down the length of each stick so that a length of No. 30 copper wire could be placed down the center of it. The copper-wire core is an essential feature of the sodium chloride electrode, for it keeps the arc directed to the center of the salt stick, whereas otherwise it would tend to follow a path in the ionized air. The sodium chloride stick was glued to the lower bolt to which one end of the copper wire was soldered. A brass-tube guide was used to keep the salt stick centered in the glass tube. A 250-watt transformer delivering 2000 volts on the secondary was used to supply energy for vaporizing the salt stick. Lower voltages were not so satisfactory for maintaining a continuous arc for long periods. It is essential that the size of the copper wire be so chosen that it will burn away at the same rate as the salt stick. The vaporizing device was operated manually. After the arc was struck, the sodium chloride was fed into the system by screwing in the lower bolt. At each setting, the stick would burn for three or four minutes, which was sufficient time for a temperature reading. The amount of salt vaporized in the stream could be easily regulated and maintained constant by varying the energy input of the transformer.

Oxygen or air was passed through the vaporizer from which the salt-laden gas passed to the mixing chamber. At the mixing chamber the gas was divided into two streams. One passed directly to the inner tube of the burner, and the other to the outer tube through a filter to remove sodium chloride dust. The filter consisted of a wad of cotton, 6 in. thick, flanged into a can 12 in. in diameter and 8 in. deep. The pressure drop through this filter was very small, and the flow through either channel was regulated by pinch clamps on the line. The procedure of premixing the gas and removing a portion of the salt vapor was necessary to insure uniformity of combustible composition in both streams.

COMPOSITION OF PITTSBURGH NATURAL GAS

The natural gas used in the experiments was taken from the laboratory supply and compressed to 1500 lb. in a large cylinder.

The average of six Orsat analyses of this gas was as follows: methane, 85.48 per cent; ethane, 13.85 per cent; nitrogen, 0.67 per cent. The maximum deviation from this average was 0.40 per cent. A sample of the gas was also subjected to a low-temperature fractionation, and the result was: methane, 88.6 per cent; ethane, 9.3 per cent; propane, 1.8 per cent; butane, 0.3 per cent; nitrogen, nil. Considering 0.67 per cent nitrogen (undetectable) as present in the methane fraction, this analysis is in satisfactory agreement with the Orsat analysis.

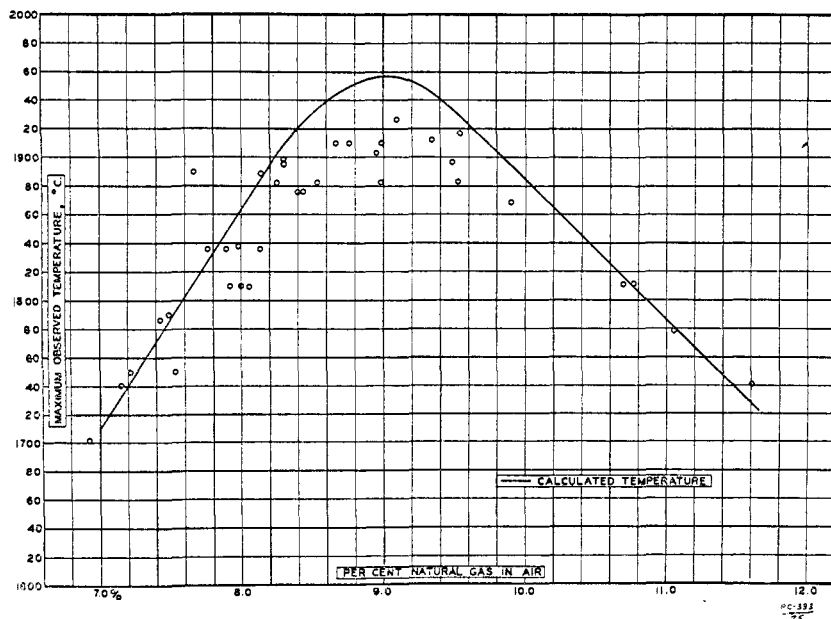


Fig. 3. Maximum observed temperatures; partially colored natural gas-air flames

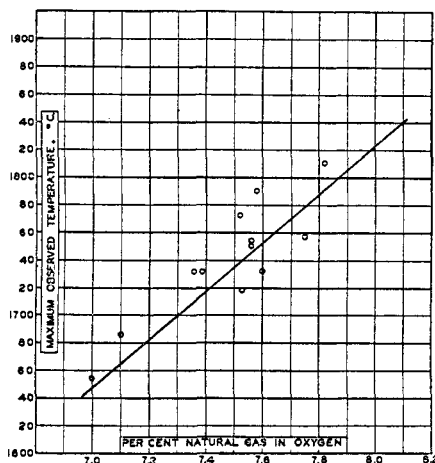


Fig. 4. Maximum observed temperatures; partially colored natural gas-oxygen flames

CALCULATED FLAME TEMPERATURES

The theoretical flame temperatures for Pittsburgh natural gas with air and with oxygen were calculated by the method outlined by Lewis and von Elbe (3), and are given by the curves in figures 3 and 4. The heats of

combustion used were those given by Rossini (5). The heat capacities and dissociation equilibria used for the temperature calculation were those compiled by Lewis and von Elbe (4) from spectroscopic data. The calculated temperature is but slightly changed if one expresses the composition of natural gas as methane and ethane rather than in terms of its true hydrocarbon content. This is the case since the respective heats of combustion are nearly the same per mole of water and carbon dioxide formed, and because the bulk of the gas is methane. The values are correct to within 2° to 4°C.

OBSERVED TEMPERATURE GRADIENTS IN FLAMES OF NATURAL GAS AND AIR

Some preliminary temperature observations were made on completely colored flames using a $\frac{3}{8}$ -in. brass tube with a grid as the burner. The observed maximum flame temperatures agreed quite well with those previously reported from this laboratory (1). As usual with completely colored flames, the observed temperatures were higher than the calculated on the rich side and lower on the lean side. There was always a positive temperature gradient above the tips of the cones, with the maximum temperature about 5 to 6 mm. above the cones. When the nitrogen in the air was replaced by oxygen, the point of maximum temperature approached the cones, and at about 50 per cent oxygen there was no vertical gradient for 1 to 2 cm. above the cones.

The effect of coloring just the central portion of the flame is shown in table 1. The temperature of the partially colored flame is considerably higher than that of a completely colored flame of the same size. The data given for the small, completely colored flame indicate that the effect of secondary air becomes greater as the flame size is reduced. The effect of partially coloring flames for line-reversal temperature measurements, as shown in table 1 (column C), is typical of the experiments reported in this paper.

As the space velocity of the combustible mixture is increased, the gradient above the cones shifts to a higher temperature range and becomes smaller, while the maximum temperature is maintained over a greater distance. This is shown in table 2.

The positive gradient above the cones of these natural gas-air flames may be explained as arising from heat losses through the grid. Relatively cold layers of gas rise in the centrally colored stream from the base of the cones near the grid enveloping the colored stream, and give rise to an observed temperature lower than the average temperature over the cross section. Owing to mixing above the cones these cold layers disappear, and the observed temperature increases. When the space velocity is increased the grid losses are decreased (table 2).

In figure 3 the maximum observed flame temperatures for various mixtures of natural gas and air are compared with calculated theoretical flame temperatures. For lean and rich mixtures the agreement between

TABLE 1
*Flame temperatures of completely and partially colored flames**

HEIGHT ABOVE CONE	TEMPERATURE		
	A	B	C
<i>mm.</i>	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$
-0.6	1654	1638	
0.0	1678	1694	1741
+0.6	1686	1710	1778
1.9	1710	1764	1810
3.2	1718	1790	1852
4.4			1882
6.4	1686	1824	1896
9.5	1615	1838	1896
12.7		1838	1896
15.9		1838	

A, completely colored flame over $\frac{3}{8}$ -in. grid; B, completely colored flame over $\frac{1}{2}$ -in. grid; C, partially colored flame over $\frac{7}{8}$ -in. grid.

* 8.52 per cent natural gas in air.

TABLE 2
*Effect of space velocity on temperature gradient and maximum temperature**

HEIGHT ABOVE CONE	$^{\circ}\text{C. FOR CUBIC FEET PER SECOND THROUGH BURNER}$				
	0.00060	0.00094	0.00119	0.00159	0.00201
<i>mm.</i>					
-1.3	1654				
-0.6	1686				
0.0	1702	1718	1726	1732	1750
+0.6	1718	1718	1832	1750	1764
3.2	1732	1732	1750	1764	1778
5.4	1718	1750	1764	1778	1778
9.5	1702	1741	1750	1778	1772
12.7				1778	1764

* 10.85 per cent natural gas in air.

observed and theoretical temperatures is very close. In the region of the maximum temperature, the observed temperatures are 20° to 40°C. below the theoretical. Table 3 permits a comparison of the temperature at the cones and the maximum observed temperature for experiments recorded in

figure 3. The temperature differences are, on the whole, smaller for the leaner mixtures. This is further evidence that heat losses are smaller for lean mixtures, as may be expected from the lower temperatures of the flames and from the greater separation of the burning zone from the grid owing to lower flame speeds.

The scattering of the experimental points in figure 3 is mainly due to the difficulty of maintaining the mixture composition constant.

TABLE 3

Difference between temperature above the cones and maximum temperature for natural gas-air flames

NATURAL GAS IN AIR	FLAME TEMPERATURE		DISTANCE ABOVE CONE	TEMPERATURE DIFFERENCE
	At cone	Maximum		
<i>per cent</i>	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	<i>mm.</i>	$^{\circ}\text{C.}$
6.51	1568	1638	3	70
7.15	1650	1741	5	91
7.22	1690	1750	9	60
7.44	1742	1786	9	44
7.54	1670	1750	9	80
7.67	1786	1890	8	104
7.77	1746	1836	9	90
7.90	1746	1836	9	90
8.00	1742	1810	9	68
8.06	1766	1810	9	44
8.13	1718	1836		118
8.14	1738	1888	10	150
8.31	1778	1898	8	120
8.53	1734	1882	6	148
8.99	1776	1910	8	134
9.35	1810	1912	9	102
9.48	1766	1896	9	130
9.55	1810	1916	9	106

EXPERIMENTS WITH NATURAL GAS-OXYGEN MIXTURES

The maximum flame temperatures for these flames were observed immediately at the cone. Above the cone the flame temperature decreased uniformly for several centimeters from this point. Since the flame speed in oxygen mixtures is faster than in air mixtures, the space velocity in these experiments was much greater. The experimental maximum temperatures are compared with the theoretical calculated temperatures in figure 4, where it is seen that the experimental points tend to be higher than the calculated. In view of the fact that heat losses occur, the negative gradient above these flames indicates the existence of excitation lag (see

preceding paper). The latter would obscure the positive gradient arising from heat losses, since these are smaller in oxygen flames owing to the high space velocity.

SUMMARY

Flame temperatures were measured by the sodium line-reversal method along the vertical axis of centrally (partially) colored Méker flames for mixtures of natural gas with air and oxygen. For air mixtures the vertical temperature gradient above the cones is positive. The temperature range and length of the positive gradient depend upon space velocity and mixture composition. In oxygen mixtures the maximum temperature is found immediately above the cones, and the vertical gradient is a uniform negative gradient for several centimeters.

The maximum observed temperatures in air mixtures show the greatest deviation from the theoretical near the stoichiometric point, being about 20° to 40°C. lower. The maximum temperatures of oxygen mixtures on the average slightly exceed the theoretical. The results are explained on the basis of heat losses, particularly to the grid, and the excitation lag in oxygen mixtures.

The authors wish to thank Doctor Guenther von Elbe for his discussions during the course of this work.

REFERENCES

- (1) JONES, LEWIS, FRIAUF, AND PERROTT: *J. Am. Chem. Soc.* **53**, 869 (1933).
- (2) KOHN: *Ann. Physik.* **44**, 749 (1914).
- (3) LEWIS AND VON ELBE: *Phil. Mag.* **20**, 44 (1935).
- (4) LEWIS AND VON ELBE: *J. Am. Chem. Soc.* **57**, 612, 2737 (1935).
- (5) ROSSINI: *J. Research Natl. Bur. Standards* **7**, 47, 329 (1931).